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On the absorption spectrum of ICl. Part I

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With 3 figures in the text

Introduction

A study of the absorption spectrum of ICl in the visible and the near infrared gives an excellent opportunity to trace the gradual change of a molecular state of high stability into its dissociation due to vibrational and rotational forces and to investigate the isotope effects due to Cl^{35} and Cl^{37}. Parts of this extensive spectrum were also investigated in numerous papers [1] in the 1930's and earlier and interpreted as transitions from the normal state $^1\Sigma^+$ into the excited states $^3\Pi_1$, $^3\Pi_0^+$, and 0^+ according to the notations given by Mulliken [2]. Part I of the present investigation is designed to extend our still rather incomplete knowledge of this representative spectrum. We believe that certain possibilities for the performance of such detailed investigations of the energy levels of rotation and vibration are given in some special improvements of the spectroscopic resolution and the method of measurements here introduced. It is our intention to continue this investigation in a second paper dealing with the irregular band structure at the limits of dissociation earlier investigated by Brown and Gibson [3]. A correlation diagram for ICl and its dissociation products as interpreted by these authors is given in Fig. 1.

Our present investigation was performed with instruments and methods somewhat unusual in common spectroscopy. It is therefore desirable first to give some details regarding the spectrograph, the separation of orders and the methods applied for the wave-number indications in the spectrum, Chaps. I—III. A comprehensive table of term-values based on the microwave constants B_0 and B_1 in the normal state $^1\Sigma^+$ is given in Chap. IV. This table includes all our measurements hitherto performed on the spectrum of ICl. The computed vibrational and rotational constants in $^1\Sigma^+$ and $^3\Pi_1$ are given in separate tables. The validity of the Morse function and of the Pekeris relation for the normal state is discussed in Chap. V. Finally, in Chap. VI the vibrational isotope effects in $^1\Sigma^+$ are computed and an accurate ϱ-value for ICl^{35}/ICl^{37} is derived by a simple method of approximation.

Chapter I

The invention of the immersion-grating [4] implies a considerable increase of spectroscopic resolution and dispersion. These improvements were earlier demon-

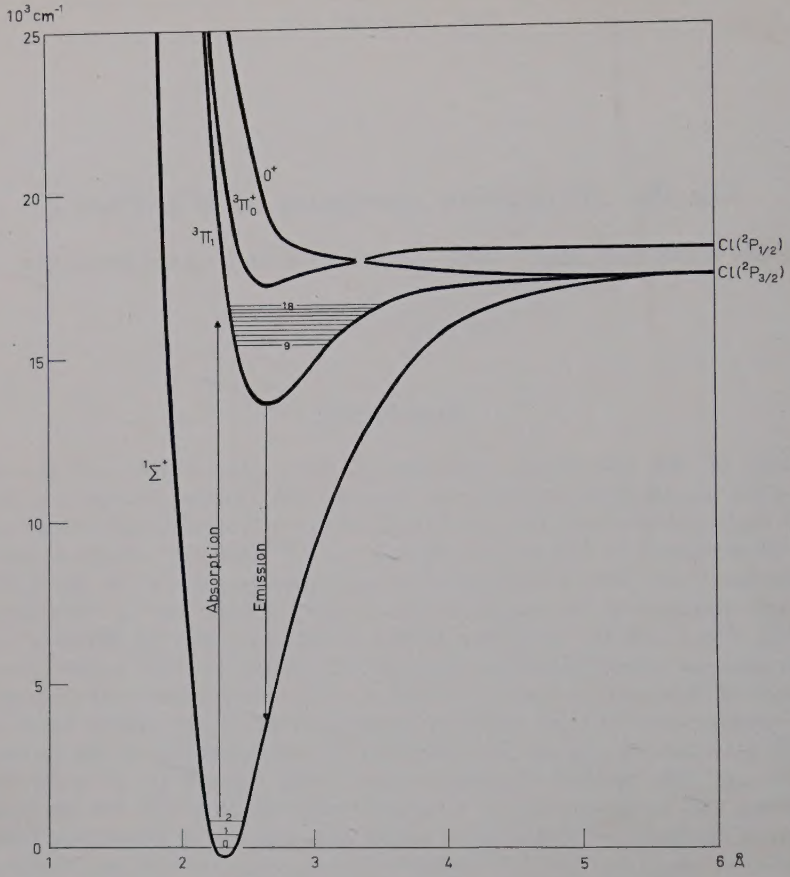

Fig. 1. Correlation diagram for ICl and its dissociation products according to Brown and Gibson [3].

strated in papers dealing with the hyperfine structure of some atomic and diatomic spectra [5].

The dispersing component of the spectrograph is composed of an aluminized plane replica-grating with 300 grooves/mm and a "ruled" area of 204×106 mm², Bausch and Lomb Catalog No. 33-53-25-85. The grating adheres by an immersion oil to the hypothenuse surface of a 30°/60° flint prism of a somewhat smaller size than the grating. As immersion oil we have used α-brome naphthalene which for years has given no sign of affecting the perishable thin plastic cover of the replica in which the ruling of the master grating is impressed. This compound grating forms a stable unit when placed on an adjustable tripod turnable around a vertical axis by a toothed wheel and helix. As shown in Fig. 2 the instrument is applied for autocollimation in a parallel beam of light produced either by (A) an achromatic telescope lens of 6 m focal length or by (B) a concave mirror of 4.5 m focal length and 15 cm aperture (B_1). In the latter case the diffracted beam from the prism-grating is focussed by a second mirror (B_2) with an aperture of

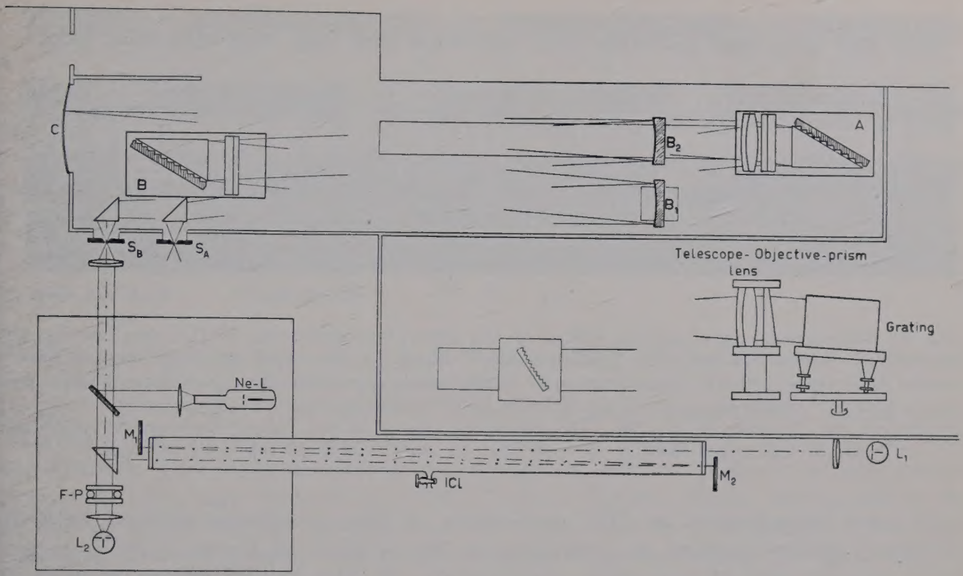

Fig. 2. Design of the spectrograph and its accessories.

S_A	Entrance-slit for the lens equipment
A	Immersion-grating in autocollimation
S_B	Entrance-slit for the concave mirror equipment
B	Immersion-grating in the Pfund-mounting
B_1	Collimating mirror
B_2	Focussing mirror
C	Photographic plate holder
L_1	Zirconium-oxide lamp
M_1, M_2	Plane mirrors for multiple passages of light through the absorption cell ICl
L_2	Sylvania lamp
F-P	Fabry-Perot etalon

33 cm [6]. Both mountings (A) and (B) are readily interchanged by shifting the table on which the compound grating is mounted as shown in Fig. 2. The entire spectrograph is mounted on stable concrete pillars in a thermally isolated room controlled by a thermometrograph.

Chapter II

Owing to the large dispersion of the spectrograph, about 0.7 cm/Å in the blazed 60° diffraction angle generally used by us, only narrow regions of the spectrum are obtainable in one exposure on a photographic plate of 20 in × 2 in. In the first place, this limitation of the spectral region introduces serious difficulties in performing accurate wavelength determinations by comparing with the sparsely distributed standard lines of Fe, Ne and A. These difficulties are

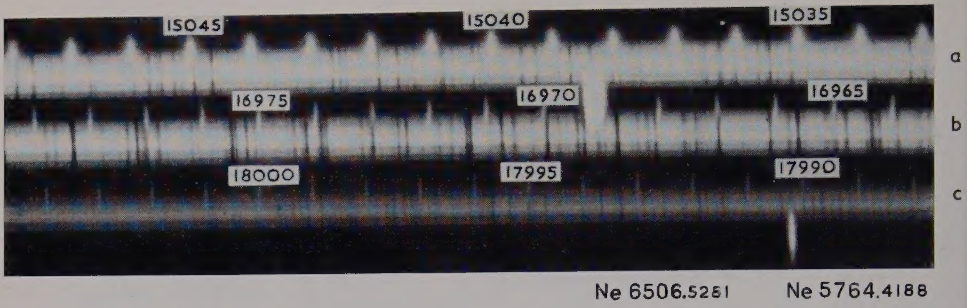

Fig. 3. Enlargement of a narrow region of the absorption spectrum of ICl obtained by the method of crossed spectra. The interferometer fringes are identified by their spectral orders $m = 2d/\lambda_{\mathrm{air}}$ where $d \approx 0.5$ cm corresponds to the plate separation in the Fabry-Perot etalon used. The F-P plates are covered by dieletric multilayers composed of 4 layers of zinc-sulphide separated by 3 layers of cryolite. The reflection power of the filters corresponds to 50 per cent in the upper shelf *a*, 60 per cent in shelf *b* and 92 per cent in shelf *c*.

still more exaggerated as the application of the coincidence method between different spectral orders m according to the relation $m_1 \lambda_1 = m_2 \lambda_2$ is no longer valid in the case of immersion spectroscopy. In the second place, the spectra produced by the compound grating contain a great number of overlapping orders $m = 12 \sim 20$ which would be rather difficult to separate from each other by means of optical filters. To overcome these difficulties two well-known methods in spectroscopy were applied.

The overlapping orders in the spectrum were separated by the method of crossed spectra [7]. For this purpose a large flint glass prism (Fig. 2) was used to separate the orders into narrow horizontal strips or "shelves" on the photographic plate as shown in Fig. 3. The 8° wedge-angle of this objective-prism was designed to include 12 to 14 orders on photographic plates of 2 inches in height. By these means 5—7 exposures covered the entire spectrum accessible within the region of transparency of the optics: 3500—12 000 Å. A narrow region of the ICl spectrum obtained by the method of crossed spectra is reproduced in Fig. 3. No deterioration of the spectral images due to the objective-prism could be observed, and on account of its practical convenience this method was thus preferred to the projection of the crossed spectrum on the slit exterior to the spectrograph.

Chapter III

A reliable scale of wavenumber marks was obtained by interference fringes according to the method of Edser and Butler [8]. These fringes were produced by filtering white light from a zirconium-oxide lamp (Sylvania) through a Fabry-Perot interferometer projecting the fringes on the spectrograph-slit. This method has been successfully tested and described in this laboratory by Pettersson [9] and by Krantz and Åslund [10], and the account given here of our application will therefore be restricted to the process of evaluating the wavenumbers.

The following equations hold for the wavelengths λ_{air} and the wavenumbers σ_{air} respectively of the interference fringes:

$$m\lambda_{\mathrm{air}} = 2d, \quad \sigma_{\mathrm{air}} = m \cdot \frac{1}{2d}, \tag{1}$$

where d is the spacing between the F-P plates and m is an integer corresponding to the spectral orders produced by the interferometer.

An approximate value of $1/2d$ is determined from two standard lines of neon with the wavenumbers σ_1 and σ_2 within one shelf on the photographic plate:

$$\frac{1}{2d} = \frac{\sigma_1 - \sigma_2}{p_1 - p_2}, \tag{2}$$

where $p_1 - p_2 = (m_1 + \varepsilon_1) - (m_2 + \varepsilon_2)$ is the number of fringe-distances and fractions of these between the two standard lines. In our case, $d \approx 0.5$ cm and $1/2d \approx 1$ cm^{-1}, $p_1 - p_2$ and $1/2d$ could be determined with 5 exact figures. This approximation was sufficient tentatively to define the integers m in (1), in our case $m \sim 16\,000$. The confirmations of the integer m implied, however, a more precise value of $1/2d$, now defined to within 7 exact figures, which corresponds to the accuracy of reading the positions on the neon lines and the fringes in the comparator. The $1/2d$-value was further controlled by extending the region of the fringes to the Ne-standards on the neighbouring shelves of the photographic plate. Finally, the σ_{air} were reduced to vacuum, n_{air} taken from Edlén's tables [11]. The wavenumbers of the bandlines were obtained from curves of dispersion graphically constructed from the positions of the fringes, and their relative errors within narrow regions of the spectrum were estimated to a few parts in 10^{-3} cm^{-1}.

For several reasons the $1/2d$-values obtained from different exposures deviate from each other by 3 or 4 parts in 10^6. In a series of 8 exposures used for our analysis the interferometer had to be readjusted a few times. Furthermore, the fringes show a faint curvature tending to alter their stooping from one end of the plate to the other. This behaviour of the fringes together with an almost invisible pending curvature of the spectrum introduces a parallactic error in the measurements. Mainly for these reasons σ-differences larger than about 30 cm^{-1} may occasionally deviate 10^{-2} cm^{-1} from their true values. Corrections within each band on the term-values in Table 2 are made for errors of this kind.

The wavelength standards of Ne were obtained from an iron hollow-cathode with neon as carrier gas, a light source invented by Crosswhite, Dieke and Salmon Legagneur [12] and tested in this laboratory by Krantz and Åslund [10]. We are indebted to Mr. H. Neuhaus for further improvements of this excellent light source.

After several failures to preserve the ICl in tubes of stainless iron an absorption cell of pyrex glass of 4.5 m length and 10 cm orifice was substituted for this. The plane end-windows of the absorption cell admit repeated passages of light through the cell necessary for the observance of the faint bands from the isotope species ICl^{37}.

The purity of ICl, indicated by the absence of the I_2-bands, was attained through repeated vacuum distillations and careful drying of the commercial product before the gas was passed into the absorption cell. Pure ICl remained for months in the pyrex tube with no sign of decomposition in spite of the intense and permanent illumination from a 100 W zirconium-oxide lamp. The remarkable preservation or restoration of the ICl gas at low pressures thus indicated will

Table 1. Combination differences and term-values of the normal state $^1\Sigma$.

ICl^{35}

$$F_0(J) = 0.113887_9\,J(J+1) - 4.04\times10^{-8}\,J^2\,(J+1)^2$$
$$F_1(J) = F_0(J) + 381.291 - 0.000535_7\,J(J+1)$$
$$F_2(J) = F_0(J) + 759.581 - 0.001071_4\,J(J+1)$$

ICl^{37}

$$F^i_0(J) = 0.109070_3\,J(J+1) - 3.70\times10^{-8}\,J^2\,(J+1)^2$$
$$F^i_1(J) = F_0(J) + 373.191 - 0.000502_0\,J(J+1)$$
$$F^i_2(J) = F_0(J) + 743.521 - 0.001004\,J(J+1)$$

J	$\Delta_2 F'$ for $v=0$		Term-values ICl^{35}			Term-values ICl^{37}		
	Observed	Calculated	F_0	F_1	F_2	F^i_0	F^i_1	F^i_2
1		0.683	0.228	381.518	759.807	0.218	373.408	743.737
2		1.139	0.683	381.971	760.258	0.654	373.842	744.169
3		1.595	1.367	382.652	760.935	1.309	374.494	744.818
4	2.051	2.051	2.278	383.558	761.838	2.181	375.362	745.682
5	2.508	2.506	3.417	384.692	762.966	3.272	376.448	746.763
6	2.965	2.960	4.783	386.051	764.319	4.581	377.751	748.060
7	3.422	3.417	6.378	387.639	765.899	6.108	379.271	749.573
8	3.875	3.872	8.200	389.452	767.704	7.853	381.008	751.302
9	4.330	4.328	10.250	391.493	769.735	9.816	382.962	753.247
10	4.782	4.783	12.528	393.760	771.991	11.998	385.134	755.409
11	5.238	5.238	15.032	396.252	774.472	14.396	387.521	757.784
12	5.694	5.694	17.766	398.973	777.180	17.014	390.127	760.378
13	6.147	6.149	20.727	401.920	780.113	19.850	392.950	763.188
14	6.604	6.605	23.915	405.093	783.271	22.903	395.989	766.213
15	7.061	7.060	27.331	408.493	786.655	26.175	399.246	769.455
16	7.514	7.515	30.975	412.120	790.265	29.664	402.718	772.912
17	7.969	7.970	34.846	415.973	794.099	33.373	406.410	776.587
18	8.426	8.426	38.945	420.053	798.160	37.298	410.317	780.476
19	8.883	8.881	43.272	424.359	802.446	41.442	414.442	784.581
20	9.340	9.336	47.826	428.892	806.957	45.803	418.783	788.902
21	9.792	9.791	52.608	433.651	811.694	50.382	423.341	793.439
22	10.246	10.246	57.618	438.638	816.657	55.181	428.118	798.194
23	10.702	10.701	62.855	443.850	821.845	60.196	433.110	803.163
24	11.156	11.156	68.318	449.288	828.542	65.429	438.319	808.348
25	11.614	11.611	74.011	454.954	832.896	70.880	443.745	813.748
26	12.065	12.066	79.930	460.845	838.759	76.549	449.388	819.365
27	12.520	12.521	86.077	466.963	844.848	82.436	455.247	825.198
28	12.975	12.976	92.451	473.307	851.162	88.541	461.324	831.247
29	13.429	13.430	99.052	479.877	857.701	94.863	467.617	837.511
30	13.886	13.885	105.882	486.675	864.467	101.403	474.127	843.990
31	14.340	14.340	112.936	493.695	871.454	108.162	481.253	850.687
32	14.795	14.794	120.221	500.946	878.671	115.137	487.798	857.598
33	15.251	15.250	127.731	508.421	886.110	122.330	494.958	864.725
34	15.704	15.703	135.470	516.123	893.776	129.742	502.336	872.068
35	16.161	16.158	143.435	524.051	901.666	137.370		
36	16.615	16.612	151.627	532.204	909.781	145.216		
37	17.069	17.066	160.046	540.584	918.121	153.280		
38	17.525	17.520	168.693	549.190	926.686	161.561		
39	17.977	17.975	177.567	558.022	935.477	170.060		
40	18.429	18.429	186.667	567.079	944.491	178.775		

Table 1 (*continued*)

J	$\Delta_2 F'$ for $v=0$		Term-values ICl^{35}			Term-values ICl^{37}		
	Observed	Calculated	$G\ (0)$	$G\ (1)$	$G\ (2)$	$G^i\ (0)$	$G^i\ (1)$	$G^i\ (2)$
41	18.882	18.882	195.995	576.363	953.731	187.709		
42	19.336	19.336	205.550	585.873	963.196	196.860		
43	19.789	19.790	215.332	595.609	972.886	206.228		
44	20.245	20.244	225.340	605.570	982.800	215.814		
45	20.698	20.698	235.575	615.757	992.938	225.617		
46	21.153	21.151	246.037	626.170	1003.302	235.637		
47	21.607	21.604	256.726	636.808	1013.890	245.875		
48	22.062	22.058	267.641	647.672	1024.702	256.328		
49	22.512	22.511	278.783	658.761	1035.739	267.000		
50	22.966	22.964	290.152	670.077	1047.001	277.888		
51	23.420	23.417	301.747	681.617		288.994		
52	23.873	23.870	313.568	693.382		300.317		
53	24.323	24.322	325.616	705.374		311.856		
54	24.776	24.776	337.891	717.591		323.612		
55	25.228	25.228	350.392	730.027		335.586		
56	25.679	25.681	363.119	742.700		348.775		
57	26.129	26.133	376.072	755.592		360.181		
58	26.582	26.585	389.251	768.708		372.805		
59	27.036	27.038	402.657	782.051		385.645		
60	27.487	27.490	416.289	795.619				
61	27.937	27.941	430.147	809.412				
62	28.392	28.392	444.230	823.428				
63	28.842	28.845	458.540	837.671				
64	29.300	29.297	473.076	852.138				
65	29.747	29.748	487.836	866.828				
66	30.197	30.200	502.823	881.745				
67	30.649	30.651	518.035	896.885				
68	31.101	31.102	533.473	912.250				
69	31.553	31.553	549.137	927.841				
70	32.005	32.004	565.026	943.655				
71	32.452	32.455	581.140	959.693				
72	32.908	32.905	597.480	975.995				
73	33.358	33.356	614.044	992.441				
74	33.806	33.806	630.835	1009.153				
75	34.256	34.256	647.850	1026.088				
76	34.725	34.706	665.090	1043.246				
77	35.155	35.156	682.555	1060.626				
78	35.603	35.605	700.245	1078.235				
79	36.038	36.055	718.160	1096.065				
80	36.505	36.505	736.299	1114.119				
81			754.662					
82			773.251					
83			792.064					
84			811.102					
85			830.364					
86			849.850					
87			869.560					
88			889.494					
89			909.652					
90			929.148					

Table 2. Term-values

$v=$	10			11			12			13		
J	c	d		c	d		c	d		c	d	
	Q	P	R	Q	P	R	Q	P	R	Q	P	R
1							15806.057			15948.090	110	
2	15503.179						06.343			48.368	365	
3	03.643			15658.337			06.779			48.794	798	
4	04.236			58.911			07.364		361	49.366	367	
5	05.009			59.637			08.090	136	107	50.086	088	089
6	05.920			60.553			08.997	983	989	50.955	950	961
7	06.975			61.598	599	598	10.009	012	028	51.970	966	967
8	08.177	182	199	62.783	789	793	11.181	189	187	53.114	118	130
9	09.547	576	561	64.128	129	137	12.499	514	507	54.407	425	421
10	11.066	059	076	65.615	626	614	13.973	978	981	55.854	859	842
11	12.730	718	745	67.262	274	276	15.583	596	590	57.432	446	442
12	14.550	541	548	69.051	052	055	17.364	355	357	59.160	176	189
13	16.520	503	529	70.996	993	001*	19.263	269	265	61.049	058	050
14	18.643	622	659	73.084	103	097	21.310	318	323	63.065	066	069
15	20.912	889	963	76.319	337	349	23.507	528	513	65.228	232	234
16	23.339	414	358	77.712	727	723	25.859	870	867	67.533	543	543
17	25.909	894	927	80.244	258	256	28.353	362	370	69.984	997	985
18	28.633	660	660	82.934	940	933	30.995	010*	022*	72.583	587	587
19	31.519	537	533	85.764	770	798	33.787	794	784	75.326	326	317
20	34.554	568	563	88.746	759	762	36.694	719	733	78.204	208	217
21	37.734	755	740	91.886	891	878	39.801	812	809	81.231	217	245
22	41.067	090	176	95.169	176	173	43.025	038	040	84.396	410	407
23	44.547	563	567	98.596	599	611	46.401	415	410	87.713	726	732
24	48.181	155	202	15702.171	184	189	49.920	930	928	91.172	189	179
25	51.963	906	970	05.899	909	911	53.582	592	595	94.774	806	779
26	55.904	920	920	09.778	794	783	57.400	409	416	98.518	530	525
27	59.986	023*	006*	13.796	812	811	61.363	370	377	16002.399	414	413
28	64.226	239	236	17.967	980	982	65.452		470	06.435	442	446
29	68.618	633	635	22.285	304	299	69.705	714	720	10.603	613	624
30	73.159	172	161	26.750	770	771	74.103	111	115	14.921	934	939
31	77.848	876	858	31.364	386	398	78	654	658	19.376	394	395
32	82.686	705	708	36.135	153	171	83.328	342	340	23.981	990	012
33	87.676	684	697	41.047	065	089	88.163	181	180	28.722	750	764
34	92.819	828	837	46.112	133	128	93.132	158		33.613	631	627
35	98.114	111	137	51.334	331	336	98.259	281	278	38.644	657	666
36	15603.536	568	574	56.670	683	695	15903.526	549	544	43.823		837
37	09.126	147	170	62.183	199	200	08.935	961	962	49.134	154	157
38	14.865	885	909	67.822	847	850	14.494	526	518	54.597	610	617
39	20.759	787	793	73.622	615	659	20.200	222	225	60.191	223	213
40	26.803	839	832	79.570	606	610	26.044	072	072	65.931	955	964
41	32.939	020*	036*	85.667	698	690	32.039	066	060	71.813	845	820
42	39.335	365	387	91.912	939	932	38.177	220	208	77.829	877	874
43	45.837	863	861	98.298	262	333	44.456	489	495	84.009	040	038
44	52.584	502	497	15804.830	874	860	50.884	913	923	90.319	357	351
45	59.259	293	295	11.515	557	550	57.453	485	485	96.772	811	804
46	66.212	228	238	18.343	388	389	64.172	199	206	16103.362	402	405
47	73.282	329	320	25.322	357	360	71.027	063	045	10.096	133	132
48	80.528	554	569	32.449	486	486	78.029	068	068	16.971	008*	014
49	87.914	946	949	39.711	732	744	85.137	207	195	23.988	027*	029
50	95.443	473	486	47.129	171	184	92.466	501	514	31.143	186	188

$^3\Pi$ state of ICl^{35}.

14			15			16			17			18		
c	d		c	d		c	d		c	d		c	d	
Q	P	R	Q	P	R	Q	P	R	Q	P	R	Q	P	R
83.854	772											16554.282		
84.251	175											54.670	691	
84.783	742	739	16213.216	226								55.189	182	188
85.444	444	447	13.908	913		16335.275	344					55.830	824	832
86.284	296	301	14.744	747		36.088	096		16450.136	137		56.597	598	589
87.280	289	288	15.713	723	721	37.044	045	050	51.061	062	069	57.501	503	488
88.412	413	405	16.821	829	828	38.121	151	123	52.114	127	121	58.527	521	531
89.686	691	701	18.069	076	077	39.344	349	353	53.310	313	320	59.688	689	692
91.102	108	104	19.456	461	433	40.704	701	709	54.631	638	633	60.969	976	973
92.656	662	660	20.977	984	989	42.190	191	203	56.091	090	092	62.391	394	391
94.354	395	355	22.638	648	649	43.819	822	815	57.670	669	676	63.931	934	932
96.196	207	206	24.446	462	457	45.577	582	580	59.391	395	396	65.647	614	604
98.174	180	184	26.384	386	390	47.474	481	478	61.234	247	245	67.407	410	406
00.298	302	308	28.462	467	468	49.505	515	514	63.207		226	69.336	339	335
02.563	565	566	30.679	684	690	51.672	680	674	65.335	328	346	71.394	396	395
04.969	982	970	33.034	038	042	53.973	978	977	67	591	578	73.571	600	585
07.506	518	527	35.529	530	536	56.406	418	108	69.943	966	959	75.894	899	898
10.197	198	226	38.157	156	162	58.981	998	015*	72.446	464		78.334	343	338
13.029	028	035	40.924	933	938	61.685	691	693	75.100	112	092	80.902	909	917
16.003	999*	001	43.832	840	842	64.528	536	541	77.875	882	881	83.601	615	614
19.100	114	111	46.877	885	887	67.500	520	512	80.767	777	797	86.427	444	422
22.354	364	366	50.062	070	078	70.620	622	631	83.789	821	821	89	394	386
25.740	752	753	53.380	392	389	73.863	873	873	86.981	986	987	92.459	475	471
29.278	285	285	56.840	851	855	77.239	255	252	90.280	286	297	95.673	684	681
32.942	932	957	60.433	455	446	80.756	772	770	93.696	703	714	99.001	027	022
36.758	771	781	64.167	175	179	84.401	407	418	97.260	276	279	16602.482	482	483
40.709	738	726	68.043	050	052	88.187	205	201	16500.951	967	953	06.051	071	072
44.804	823	820	72.045	074	058	92.102	122	119	04.761	786	786	09.769	794	790
49.029	038	050	76.191	209	205	96.156	174	170	08.718	737	743	13.610	633	637
53.416	425	421	80.477	496	492	16400.338	359	363	12.798	820	816	17.576	608	603
57.921	941	948	84.899	922	918	04.660		676	17.013	030	029	21.672	703	698
62.578	603	596	89.449	463	480	09.109	131	127	21.348	372	376	25.896	929	927
67.377	394	395	94.144	156	168	13.698	721	717	25.822	861	845	30.248	276	274
72.311	329	332	98.971	982	995	18.408	436	440	30.419	445	447	34.726	754	752
77.379	410	411	16303.933		964	23.266	292	294	35.153	179	183	39.324	356	360
82.596	615	618	09.028	053	076	28.254	280	282	40.013	045	046	44.050	084	089
87.945	961	970	14.267	295	304	33.367	408	399	45.000	048	036	48.901	937	937
93.433	446	462	19.647	673	681	38.625	657	649	50.124	158	159	53.878	915	917
99.066	092	106	25.157	179	192	44.013	037	042	55.370	407	402	58.982	021*	018*
04	862	869	30.816	836		49.522	553	558	60.747	788	787	64.207	248	248
10.736	772	768	36.596	616	618	55.172		209	66.251	293	295	69.559	608	608
16.785	821	821	42.500	541	537	60.964	975	993	71.886	925	932	75.032	081	080
22.968	000*	002*	48.559	595	599	66	896	907	77.649	694	696	80.634	680	685
29.289	336	338	54.748	788	797	72.902	949	951	83.544	588	575	86.358	403	406
35.762	802	795	61.075	114	112	79.078	124	140	89.559	597	603	92.211	262	265
42.357	405	399	67.536	572	581	85.381	434	440	95.709	754	758	98.179	218	239
49.096	144	141	74.134	182	186	91.825	870	881	16601.986	030*	042*	16704.279	330	340
55.973	021*	021*	80.864	898	909	98.398	449	447	08.377	441	435	10.486	363	561
62.988	045*	035*	87.722	764	770	16505.101	160	148	14.905	968	966	16.831	894	903

Table 2 (*continued*)

v =	10			11			12			13		
	c	*d*		*c*	*d*		*c*	*d*		*c*	*d*	
J	*Q*	*P*	*R*	*Q*	*P*	*R*	*Q*	*P*	*R*	*Q*	*P*	*R*
51	15703.122	160	170	54.693	738	742	99.937	929	941	38.442	489	48
52	10.957	996	006*	62.398	451	447	16007.526	505	521	45.878	927	92
53	18.938	984	984	70.255	302	291	15.190	234	242	53.458	520	50
54	27.064	116	097	78.255	303	296	23.054	093	102	61.175	229	23
55	35.347	390	400	86.406	448	451	31.059	111	108	69.032	091	09
56	43.780	825	858	94.690	740	741	39.209	275	258	77.037	085	08
57	52.347	372	399	15903.129	180	183	47.497	556	553	85.173	241	22
58	61.068	107	129	11.712	768	780	55.929	997	991	93.443	514	50
59	69.946	988	999	20.441	485	498	64.511	531	564	16201.866	924	93
60	78.955		003*	29.314		371	73.259	302	294	10.421	487	49
61	88.112	191	179	38.330	396	398	82.094	165	156	19.123	182	18
62	97.427		490	47.495	562	560	91.083	158	159	27.951	023*	01
63	15806.895			56.802	879	846	16100.245	301	295	36.928	996	99
64	16.508			66.244	302	325	09.531	585	594	46.055	111	11
65				75.850	938	916	18.953	046	021	55	367	36
66				85.593	595	662	28.526	608	583	64.680	756	75
67				95.476		544	38.233	301	311	74.203	279	28
68				16005.437		576	48.092	159	157	83.868	944	
69				15.673		733	58.076	147	163	93.672	749	74
70				25.988			68.195	279		16303.606	691	70
71				36.450			78.470	561	559	13.682	771	76
72				47.037			88.891	964	956	23.889	984	98
73				57.773			99.435	521	523	34.245	340	34
74				68.671			16210.137	213	219	44.731	820	
75				79.703			20.951	033*	061*	55.349	439	
76				90.864			31.928	024*	045*	66.107	256	
77				16102.171			43.035	130	153	76.990		
78				13.642			54	379	378	88.022		
79							65.670	785	765	99.185		
80							77.200		264	16410.486		
81							88.865	969	978	21.915		
82							16300.662	770	775	33.492		
83							12.595	738	716	45.182		
84							24.675	826	779			
85							36.890		925			
86							49.234					
87												
88												
89												
90												

be discussed in relation to our analysis of the predissociation phenomena exhibited by the excited states $^3\Pi_0^+$ and 0^+.

Chapter IV

The rotational constants of ICl in the states here considered were computed graphically from the relations

14			15			16			17			18		
c	*d*		*c*	*d*		*c*	*d*		*c*	*d*		*c*	*d*	
Q	*P*	*R*	*Q*	*P*	*R*	*Q*	*P*	*R*	*Q*	*P*	*R*	*Q*	*P*	*R*
70.142	192	199	94.718	770	764	11.930	986	990	21.561	629	663	23.297	363	
77.434	483	487	16401.856	906	924	18.895	949	951	28.346	410	408	29.879	956	965
84.861	919	906	09.113	158	169	25.989	050*	027*	35.251	317	326	36.593	670	702
92.424	476	484	16.517	568	590	33.212	280	278	42.288	359	342	43.423	501	523
300.126	179	187	24.043	117	110	40.564	630	638	49.447	525	523	50.378	461	462
07.958	008*	003*	31.715	785	779	48.051	127	127	56.736	807	811	57.452	523	538
15.937	020*	000*	39.514	574	587	55.662	743	735	64.146	235	220	64.648	734	711
24.045	111	124	47.449	512	525	63.407	488	478	71.686	778	770	71.965	061*	057*
32.296	358	354	55.516	594	584	71.279	355	352	79.323	428	426	79.401	516	496
40.680	755	741	63.714	798	789	79.280	351	357	87.138	222	220	86.963	056*	056*
49.204	262	262	72.047	140	129	87.407		487	95.050	142	134	94.638	737	720
57.853	930	919	80.510	586	588	95.659	731		16703.081		169	16702.450	544	543
66.640	711	710	89.097	183	192	16604.034	105	145	11.239	324	341	10.347	456	465
75.562	663	654	97.832		918	12.553	636	650	19.499	616	609	18.377	498	492
84.629	699	712	16506.689	777	785	21.194	281	280	28	016	031	26.540	652	650
93.826	905	900	15.677	762	746	29.974	055*	046*	36.449	549	523	34.799	931	926
403.184	229	222	24.800	902	869	38.855	954	951	45.097	215		43.262	351	314
12.612	706	707	34.043	141	142	47.877	976	975	53.869	003*	993	51.890	816	820
22.218	348	307	43.423	517		57.026	128	138	62.762	883	885	60.595	448	453
31.946	036*	038*	52.936	029*	045	66.297	398	401	71.783	902	904	69	199	198
41.810	908	949	62.582	682	678	75.693	851	819	80.922	045*	045*	78.254	054	035
51.807	907	912	72.344	454	473	85.219	324	336	90.178	311	317	87.321	051	033
61.941	033*	043*	82.243	359	357	94.867	960	003*	99.561	698	695	96	116	119
72,205	310	327	92.274	407	382	16704.645	765	773	16808.994	191*	192*	16805	331	320
82.606	703	709	16602.429	540	541	14.541	667	669	18.680	822	818	14	708	647
93.151	239	247	12.717	843	837	24.559	667	698	28.414	544	564	24		130
503.835	951	907	23.123	253	252	34.711	847	823	38.290	395	431	33	620	652
14.619	763	744	33.648	803	797	44.977	126	116	48.233	393	402	43	338	302
25.513	694	719	44.342	480	477	55.378	521	482	58.334	491	513	53	077	074
36.570	831	797	55.121	282	287	65.896	029*	070*	68.543	721	702	63	010	014
47.752	987	028*	66.055	259	161	76.527	673	747	78.874	042*		73	018	985
59.068		446	77.104	318	253	87.285	448	488	89.329	506	477	83	069	045
70.520		951	88.307		422	98.162		442	99.881	060*	062*			
82.100		554	99.597		727	16809.164		466	16910.558					
93.814		211*	16711.024		125	20.265			21.330					
605.641			22.558		724	31.530			32.238					
17.612			34.235			42.930			43.283					
29.704			46.046		254	54.464			54.428					
41.920			57.963											
53.417														

$$\Delta_2 F'' = R(J-1) - P(J+1) = (4B - 6D)\ (J+\tfrac{1}{2}) - 8D(J+\tfrac{1}{2})^3 \qquad (3)$$

for the normal state $^1\Sigma^+$ $v = 0, 1$ in ICl^{35}, and $v = 0$ in ICl^{37}, and similarly from $\Delta_2 F' = R(J) - P(J)$ for the excited states $^3\Pi_1(d)$ $v = 10$–18 in ICl^{35} and $v = 16$–18 in ICl^{37}. The means of $\Delta_2 F''$ from 9 bands for the normal state $v = 0$ in ICl^{35} are tabulated in the second column of Table 1. The less accurate mean values of $\Delta_2 F''$ from 3 bands ending on $^1\Sigma^+$ $v = 1$ are not given. The constants

Table 3. Term-values of the $^3\Pi_1$ state of ICl^{37}.

J	11 *c* *Q*	12 *c* *Q*	13 *c* *Q*	14 *c* *Q*	15 *c* *Q*	16 *c* *Q*	17 *c* *Q*	18 *c* *Q*
1								
2						16295.666		
3						96.052	16410.337	
4	15625.414			16047.466	16175.389	96.551	10.839	16517.950
5	26.142	15772.987	15913.717	48.140	76.048	97.227	11.481	18.555
6	26.999		14.544	48.968	76.855	98.012	12.244	19.321
7		74.825	15.520	49.909	77.798	98.927	13.142	20.198
8	29.144	75.957	16.631	51.000	78.862	99.975	14.164	21.199
9	30.445		17.879	52.230	80.065	16301.151	15.309	22.318
10	31.873		19.263	53.598	81.398	02.462	16.593	23.567
11			20.787	55.101	82.870	03.898	17.992	24.944
12	35.169	81.890	22.466	56.733	84.472	05.469	19.536	26.427
13	37.030	83.727	24.261	58.506	86.214	07.165	21.195	
14	39.044	85.711	26.204	60.418	88.084	09.000	22.985	29.792
15	41.205	87.822	28.297	62.468	90.088	10.967	24.899	31.659
16	43.496	90.096	30.511	64.643	92.225	13.058		33.649
17	45.940	92.478	32.875	66.958	94.495	15.293	29.117	35.769
18	48.514	95.013	35.368	69.413	96.901	17.631	31.418	38.010
19	51.247	97.702	38.006	72.012	99.436	20.113	33.838	40.375
20	54.111	15800.520	40.784	74.721	16202.105		36.395	42.861
21	57.116	03.489	43.691	77.584	04.909	25.482	39.072	45.472
22	60.264	06.593	46.737	80.583	07.844	28.346	41.879	48.211
23	63.568	09.839	49.929	83.712	10.917	31.350	44.811	51.069
24	67.000	13.220	53.259	86.968	14.108	34.489	47.855	54.055
25	70.592	16.744	56.736	90.385	17.444	37.745	51.061	57.162
26	74.308	20.415		93.912		41.140	54.384	60.388
27	78.176	24.222		97.591		44.666	57.816	63.743
28	82.193	28.168		16101.408		48.319	61.386	67.221
29	86.348	32.192		05.346		52.104	65.078	70.817
30	90.640					56.012	68.884	74.543
31	95.078					60.058	72.848	78.385
32	99.664					64.228	76.919	82.355
33	15704.387					68.529	81.119	86.443
34	09.232					72.973	85.441	90.649
35	14.163						89.895	94.990
36	19.403					82.192	94.470	99.452
37	24.703					87.012	99.177	16604.027
38	30.157					91.949	16504.001	08.728
39	35.719					97.022	08.952	13.551
40	41.437					16402.235	14.035	18.494
41	47.304					07.562	19.922	23.585
42	53.289					12.960	24.061	28.252
43	59.445					18.601	30.003	34.056
44	65.736					24.344	35.583	39.478
45	72.151					30.153	41.287	45.028
46	78.722					36.129	47.111	50.697
47	85.437					42.223	53.059	56.492
48	92.284							62.395
49	99.272							68.430
50	15806.412							74.579
51	13.677							80.847
52	21.094							87.247
53	28.655							93.744
54	36.343							16700.371
55	44.184							07.114

of this state will, however, be derived by a more accurate method given at the end of this chapter.

Townes *et al.* [13] have computed the constants of $^1\Sigma^+$ $v=0$ and $v=1$ from their very exact measurements of the pure rotational transition $J=3 \rightarrow J=4$ in the microwave region. Owing to the spin and the quadrupole moments of the nuclei this "line" is split into a considerable number of hyperfine structure components, for a single isotopic species into about 150 components, completely unresolved by optical means. Their rotational constants B_0 and B_1 for ICl^{35} and ICl^{37} are here recalculated in terms of wavenumbers, using the new values for the velocity of light [14], $c=2.99792\times10^{10}$ cm/sec.

$$\begin{array}{rr} ICl^{35} & ICl^{37} \\ B_0=0.113887_9 \text{ cm}^{-1} & B_0^i=0.109070_3 \text{ cm}^{-1} \\ B_1=0.113352_2 \text{ cm}^{-1} & B_1^i=0.109201_0 \text{ cm}^{-1} \\ a=B_0-B_1=0.000535_7 \text{ cm}^{-1} & a^i=0.000502_0 \text{ cm}^{-1} \end{array}$$

From their B_0-values and using an estimated value for $D_0=4.04\times10^{-8}$, the $\Delta_2 F''$ and the rotational term-values for $^1\Sigma^+$ $v=0$ in ICl^{35} are calculated in columns 3 and 4 respectively in Table 1. Similarily, the term-values for $^1\Sigma^+$ $v=0$ in ICl^{37} are given in column 7.

Although the agreement between our observations and the calculated $\Delta_2 F''$ in the columns 2 and 3 is rather good, it will be noted that an error in the D-values accepted may introduce systematic errors in the term-values of column 4 amounting to a few parts in 10^{-2} cm^{-1} at $J\sim80$. Such errors will, however, be of no importance in the use we intend to make of these tables.

Searching for still higher correction terms such as β_e and H_e in $D_v=D_e+\beta_e(v+\frac{1}{2})$ and $H_e J^3(J+1)^3$ respectively, these were found to be negligibly small. Dunham's theory [15] for the vibrating rotor applied in our case gives

$$\beta_e\sim0.0046\ D_e \quad \text{and} \quad H_e\sim1\times10^{-14}.$$

Our computed term-values for the normal states therefore form a reliable basis for the construction of the term-values for the excited states given in Tables 2 and 3. We have here proceeded in the following way.

The d and c components of the vibration levels $v=10$–18 in $^3\Pi_1$ were computed by adding the observed wavenumbers of $P(J)$, $R(J)$ and $Q(J)$ to their corresponding term-values in $^1\Sigma^+$ $v=0$. Thus the d-component appears as a fictitious doublet due to the errors in $P(J+1)$ and $R(J-1)$. This procedure was chosen with the aim of preserving the original wavenumbers. Attention must also be paid to the errors in the columns of term-values in $^3\Pi_1$ referred to in Chap. III, which occasionally may amount to ±0.02 cm^{-1}.

In order to make use of the strong and reliable Q-branches represented by

$$Q(J)=\nu_o+({}_cB_v'-B_v'')\ J\ (J+1)-({}_cD_v'-D_v'')\ J^2\ (J+1)^2, \tag{4}$$

ν_o is calculated by inserting the computed values for ${}_dB_v'$ and ${}_dD_v'$ in the equation:

$$\nu_o+xJ(J+1)+yJ^2(J+1)^2=Q(J)-({}_dB_v'-B_v'')\ J\ (J+1)+({}_dD_v'-D_v'')\ J^2\ (J+1)^2.$$

By using the ν_o's thus obtained more accurate values ${}_cB_v'$ and ${}_cD_v'$ are then computed by graphical methods.

Our information regarding the term-values and the rotation constants B_1 and B_2 of $^1\Sigma^+$ $v=1$ and $v=2$ are mainly based on the measurements of Q-branches ending on $v=1$ and 2. For the sake of convenience designating these branches Q_1 and Q_2 respectively their relations to the Q_0-branches ending on $v=0$ are given by

$$\left.\begin{aligned} Q_0(J)-Q_1(J)&=G(1)-G(0)+(B_1-B_0)\;J\;(J+1)+\;\cdots\\ Q_0(J)-Q_2(J)&=G(2)-G(0)+(B_2-B_0)\;J\;(J+1)+\;\cdots \end{aligned}\right\}, \tag{5}$$

where $G(1)-G(0)$ and $G(2)-G(0)$ correspond to the term-values for the vibration states at $J=0$. When these differences are plotted graphically to $J(J+1)$, straight curves are obtained up to $J\sim 80$, which confirms our earlier estimation regarding the negligible β-coefficients in $\beta J^2(J+1)^2$.

Thus we find

$$\mathrm{ICl}^{35}\;\left\{\begin{aligned} B_0-B_1&=0.000535\pm 0.000001\\ B_0-B_2&=0.001067\pm 0.000002, \end{aligned}\right.$$

$$\mathrm{ICl}^{37}\;\left\{\begin{aligned} B_0-B_1&=0.000502\\ B_0-B_2&=0.001004. \end{aligned}\right.$$

Inserting these values in the general formula

$$B_v=B_e-\alpha_e\,(v+\tfrac{1}{2})+\gamma_e\,(v+\tfrac{1}{2})^2,$$

the following constants are derived:

$$\begin{aligned} &\mathrm{ICl}^{35}:\quad B_e=0.114154_4,\quad \alpha_e=0.000533_6,\quad \gamma_e=0.000001_2;\\ &\mathrm{ICl}^{37}:\quad B_e^i=0.109321,\quad \alpha_e^i=0.000502,\quad \gamma_e^i\approx 0. \end{aligned}$$

Our B_0-B_1 are in excellent agreement with the corresponding values derived from the microwave measurements. This should be emphasized here, as the microwave values are based on observations on single frequencies interpreted as originating from the vibrational state $v=1$. Finally the rotational and the vibrational constants for the excited state $^3\Pi_1$ are given in Tables 4 and 5.

Chapter V

The vibrational levels in the normal state $^1\Sigma^+$ of ICl^{35} are known with some accuracy, ~ 0.1 cm^{-1}, for $v=0$, 1 and 2 from the work of Curtis and Patkowski [16]. Within more uncertain limits of error Darbyshire [17] states that the $G(v)$'s decrease linearly for $v<7$ and approximately according to $\omega_e x_e \sim 1.5$ cm^{-1}. The excited $^3\Pi_1$ offers far better possibilities for an extensive investigation of its vibration levels. Thus the transitions $^1\Sigma^+$ $v''=0, 1, 2 \rightarrow {}^3\Pi_1\,v'$ appear as strong progressions of bands which can be followed from $v'=0$ up to their actual convergence at $v'\approx 35$, 36. This happens at ~ 5730 Å corresponding to a dissociation limit situated $\sim 17\,300$ cm^{-1} above $^1\Sigma^+$ $v=0$. These intensity relations are immediately understood by applying the Franck-Condon principle to the transition $^1\Sigma^+ \rightarrow {}^3\Pi_1$ illustrated by the potential curves in Fig. 1.

However, if the $G(v)$'s of the normal state are extrapolated according to

$$G(v)=384\,(v+\tfrac{1}{2})-1.5\,(v+\tfrac{1}{2})^2,$$

Table 4. Rotational constants of the excited state $^3\Pi_1$ in ICl^{35} and ICl^{37} from graphical computations.

	$_dB$	$_cB$	Δ_cB	$_dD \times 10^8$	$_cD \times 10^8$
			ICl^{35}		
10—0	0.07578	0.07582_1	0.00116_4		9.7
11—0	0.07468	0.07465_7	121_3	10.3	10.1
12—0	0.07344	0.07344_4	128_5	10.9	11.0
13—0	0.07218	0.07215_9	136_7	12.2	12.0
14—0	0.07085	0.07079_2	145_1	13.4	13.0
15—0	0.06938	0.06934_1	153_8	14.6	14.3
16—0	0.06783	0.06780_3	164_7	15.9	15.6
17—0	0.06620	0.06615_6	175_7	18.4	17.7
18—0	0.06444	0.06439_9		20.4	19.7
19—0	0.06259			23.2	
9—1		0.07691_8			8.7
13—1	0.07218	0.07214_0	0.00135_6	11.9	11.4
14—1	7081	0.07078_4	144_0	12.9	12.9
15—1	6936	0.06934_4		14.2	14.3
			ICl^{37}		
16—0	0.06558	0.06552_4		17.8	15.1
17—0	0.06396	0.06402_9	0.00149_5	17.3	17.3
18—0	0.06233	0.06241_4	0.00161_5	15.6	18.5

Table 5. The zero lines ν_0 of some bands of $^3\Pi_1 - {}^1\Sigma^+$ from graphical computations.

$v' \diagdown v''$	0	1	2	$G(v) - G(0)$
		ICl^{35}		
9		14960.725		
10	15502.724			
11	15657.407		14897.826	759.581
12	15805.893			
13	15947.918	15566.617		381.301
14	16083.315	15702.025		290
15	16211.830	15830.551		279
16	16333.242	15951.961		281
17	16447.357	16066.061		296
18	16553.895	16172.616		279
		ICl^{37}		
11	15623.986		14880.465	743.521
12	15770.872			
13	15911.628	15538.418		373.210
14	16046.097	15672.902		195
15	16174.051	15800.867		184
16	16295.263	15922.086		177
17	16409.561	16036.376		185
18	16516.711	16143.503		208

their limit of convergence is found to lie at 23 300 cm^{-1}, that is ~6000 cm^{-1} above the limit of dissociation stated above. Maintaining the correlation given in Fig. 1 regarding the atomic and the molecular states, one may therefore suppose that some kind of interaction takes place between the vibration levels at $v \sim 50$ in $^1\Sigma^+$ and the $^3\Pi$-states due to overlapping wave-functions, especially in the region of their r-maxima. These interactions may not necessarily produce rotational perturbations, but only small shifts at low J-values leading to the appearance of vibrational perturbations of the type found by Herzberg in P_2. Actually perturbations were reported by Darbyshire and by Curtis at $v=10$ and $v=17$ in $^3\Pi_1$, and they will be discussed in greater detail in Part II.

In order to destrict the present discussion to the minimum of the potential curve in $^1\Sigma^+$ holding the vibration levels $v=0$, 1 and 2, this can be represented to a very high degree of accuracy by the Morse function [18]:

$$U(r-r_e)=\frac{\omega_e^2}{4\,\omega_e x_e}\left[1-e^{-\beta(r-r_e)}\right]^2, \tag{6}$$

where

$$\beta=\omega_e x_e \times \left(\frac{\pi\, e\, m}{\hbar}\right)^{\frac{1}{2}}.$$

In order to remove the arbitrariness of this function its three parameters ω_e, $\omega_e x_e$ and $B_e(r_e)$ must be related with each other by a fourth parameter, suitably represented by the interaction constant α_e. According to Pekeris [19] this relation is given by

$$\alpha_e=6\,\frac{B_e}{\omega_e}\left[(B_e\,\omega_e x_e)^{\frac{1}{2}}-B_e\right]. \tag{7}$$

Using our new values (ω_e and $\omega_e x_e$ in Chap. VI) of these parameters, we find

in ICl^{35} α_e (calc.) = 0.000534, in ICl^{37} α_e (calc.) = 0.00050,

which is in excellent agreement with the observed values given in Chap. IV. The agreement between the Morse function and our observations at low vibrational levels in $^1\Sigma^+$ here demonstrated does not imply any assumption of its general validity. There are some representative cases known of its complete failure, e.g. the normal state of H_2 discussed by Rydberg [20]. From an extensive comparision between the Morse fuction and its generalization by Pöschl and Teller [21] recently given by Beckel [22] it appears, however, that there is still a large group of well-known diatomic spectra obeying the Morse function to within a few per cent of error in (7), some of these deviations falling within the uncertainties of present data regarding α_e and $\omega_e x_e$.

Chapter VI

The rotational isotope effects in ICl^{35} and ICl^{37} have been thoroughly discussed by Townes *et al.*, who have arrived at a very accurate value for the mass ratio between the chlorine isotopes

Table 6. Some ΔG for the normal state $^1\Sigma^+$ in ICl^{35} and ICl^{37}.

v'	13	14	15	16	17	ΔG (mean)
$G(1)-G(0)$ $G^i(1)-G^i(0)$	381.310 373.210	381.296 373.195	381.275 373.176	381.282 373.184	381.290 373.189	381.291 373.191
$\Delta G-\Delta G^i$	8.100	8.101	8.099	8.098	8.101	8.100

$$\frac{M(\mathrm{Cl}^{35})}{M(\mathrm{Cl}^{37})}=0.9459801\pm 50\times 10^{-7}$$

as compared with the reliable value $0.9459803\pm 15\times 10^{-7}$ obtained with the microwave-molecular beam method on KCl [23]. It will also be noticed here that the appearance of $\gamma_e(v+\frac{1}{2})^2$ in the expansion of the molecular energy levels as shown above in Chap. IV will change the mass ratio found in ICl only very slightly (0.945805). From these viewpoints it is of interest to combine our data regarding the vibrational isotope effects in the normal state $^1\Sigma^+$ represented by

$$G(v)=\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2.$$

Correspondingly
$$G(1)-G(0)=\omega_e-2\,\omega_e x_e, \tag{8 a}$$
$$G(2)-G(0)=2\,\omega_e-6\,\omega_e x_e \tag{8 b}$$

are applied to the relations given in (5). Our computed vibrational constants are

$$\omega_e=384.293,\quad \omega_e x_e=1.501,$$
$$\omega_e^i=376.065,\quad \omega_e^i x_e^i=1.437.$$

Some ΔG available from our measurements are given in Table 6. The close agreement between the $\Delta G-\Delta G^i\approx 8.100\ \mathrm{cm}^{-1}$ arises from the fact that the related isotope bands are closed to each other. Although the deviations among the ΔG-values are large their ratios will not be seriously affected hereby.

In order to calculate $\varrho=(\mu_{35}/\mu_{37})^{\frac{1}{2}}$ from the mean values for $\Delta G(1)$ and $\Delta G^i(1)$ in (8 a) we proceed as follows:

$$G(1)-G(0)=\omega_e-2\,\omega_e x_e,$$
$$G^i(1)-G^i(0)=\varrho\,\omega_e-2\,\varrho^2\,\omega_e x_e,$$

and consequently
$$\varrho=\frac{G^i(1)-G^i(0)-2\,\varrho\,(1-\varrho)\,\omega_e x_e}{G(1)-G(0)}.$$

Approximating
$$2\,\varrho\,(1-\varrho)\,\omega_e x_e\approx 0.063\ \mathrm{cm}^{-1},$$

we find
$$\varrho=0.978591\pm 10\times 10^{-6},$$

which is in close agreement with the corresponding microwave value $\varrho=0.978595$.

From one available and less reliable pair of $G(2)-G(0)$ values computed from the Q-branches in the 11–0 and 11–2 bands, $G(2)-G(0)=759.581$ and $G^i(2)-G^i(0)=743.521$ (Table 5), we find similarly applying (8 b)

$$\varrho = 0.97861.$$

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REFERENCES

1. Detailed references are given in HERZBERG, G., Spectra of Diatomatic Molecules, D. Van Nostrand Co., New York, Second Edition, 1951.
2. MULLIKEN, R. S., Rev. Modern Physics, *4*, 17, 70 (1932)
3. BROWN, W. G., and GIBSON, G. E., Phys. Rev. *40*, 529 (1932).
4. HULTHÉN, E., Arkiv f. Fysik, *2*, 439 (1950).
   HULTHÉN, E., and NEUHAUS, H., Arkiv f. Fysik, *8*, 343 (1954).
5. HULTHÉN, E., and NEUHAUS, H., Phys. Rev. *102*, 1415 (1956).
   BJÖRKLUND, O., Arkiv f. Fysik, 13, 185 (1958).
   NEUHAUS, H., Z. Physik, *150*, 4 (1958).
6. PFUND, A. H., J. O. S. A. *22*, 281 (1932).
7. HARRISON, G. R., J. O. S. A., *39*, 522 (1949).
8. EDSER, E., and BUTLER, C. P., Phil. Mag., *5. ser. 46*, 207 (1898).
9. PETTERSSON, A. V., Arkiv f. Fysik. *10*, 109, (1955).
10. KRANTZ, B.-Å., and ÅSLUND, N., Arkiv f. Fysik *10*, 165 (1956); *11*, 453 (1956).
11. EDLÉN, B., Corrections to Kayser's "Tabelle der Schwingungszahlen", J. Opt. Soc. A. *43*, 339 (1953).
12. CROSSWHITE, H. N., DIEKE, G H., and LEGAGNEUR, C. S., J. O. S. A., *45*, 271 (1955).
13. TOWNES, C. H., MERRITT, F. R., and WRIGHT, B. D., Phys. Rev., *73*, 1334 (1948).
    See also: TOWNES, C. H., and SCHAWLOW, A. L.: Microwave Spectroscopy, Mc Graw-Hill Publ., New York (1955).
14. BERGSTRAND, E., Arkiv f. Fysik, *2*, 119 (1950).
15. DUNHAM, J. L., Phys. Rev. *41*, 721 (1932).
16. CURTIS, W. E., and PATKOWSKI, J., Phil. Trans. Roy Soc., *232*, 395 (1934).
17. DARBYSHIRE, O., Phys. Rev., *40*, 366 (1932).
18. MORSE, P. M., Phys. Rev., *34*, 57 (1929).
19. PEKERIS, C. L., Phys. Rev., *45*, 98 (1934).
20. RYDBERG, R., Dissertation, Stockholm (1935).
21. PÖSCHL, G., and TELLER, E., Z. Physik, *83*, 143 (1933).
22. BECKEL, C. L., J. Chem. Phys., *27*, 998 (1957).
23. LEE, C. A., FABRICAND, B. P., CARLSON, R. O., and RABI, I. I., Phys. Rev. *91*, 1395 (1953).

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